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# Deep ultraviolet and visible crystalloluminescence of sodium chloride

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A protocol has been developed for production of intense crystalloluminescence (XTL) from sodium chloride in aqueous solution by selective doping with transition metal salts ( $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Dy}^{3+}$ ). The method was used to record complete, fully dispersed deep UV–visible (200–650 nm) XTL spectra of sodium chloride for the first time. The results show conclusively that the emissions are due to dopant cations in the NaCl lattice, with no evidence for emission directly from NaCl, e.g., by triboluminescence resulting from crystalline fracture. The UV components of the XTL spectrum are attributed to single cation substituents ( $\text{Ag}^+$  and  $\text{Cu}^+$ ), and a strong visible component ( $\sim 415$  nm) of the XTL is attributed to emission from silver-pair centers,  $(\text{Ag}^+)_2$ . The nature of the electronic transitions of the dopant cations is discussed. The results suggest that the timescale for transformation of a cluster to the crystalline phase is rapid, with efficient relaxation to the lowest excited electronic states of the dopant cation. This transformation is followed by photoemission of the cation in the nascent crystal. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3684548>]

## I. INTRODUCTION

Crystalloluminescence (XTL) is the emission of light during crystallization.<sup>1</sup> It can be distinguished from more widely known forms of luminescence, such as chemiluminescence (CL) or triboluminescence (TL), although in many cases the apparent XTL can be linked back to one of these other mechanisms.<sup>2,3</sup> Observations of the phenomenon of XTL dates as far back as 1787, where Pickel reported seeing a bright emission of light during the solidification of fused potassium sulfate.<sup>4</sup> Bandrowski in 1894 was the first to report XTL by precipitation of sodium chloride from solution using hydrochloric acid.<sup>5</sup> The first systematic study of NaCl was carried out by Weiser, who studied various physical parameters (e.g., pH, stirring, viscosity) and attempted to quantify these effects on the XTL.<sup>6</sup> A large number of examples of XTL have since been discovered, and are summarized in an excellent review by Barsanti and Maccarrone.<sup>1</sup> Even with such a long history of research, XTL appears to have remained a fascinating but obscure phenomenon: this is surprising, since XTL emission acts as a potential marker for the critical act of nucleation.<sup>7,8</sup> XTL has recently been suggested as a source of light in deep-ocean hydrothermal vents, although the light levels were deemed to be lower than that required for full photosynthesis.<sup>9</sup>

Due to the availability of reagents and the relative ease of preparation, rapid crystallization of aqueous sodium chloride has been the most popular system of XTL for study. The XTL of NaCl can be observed by adding a concentrated HCl solution to a near-saturated salt solution, causing rapid precipitation of the salt. Mixing of concentrated NaOH and HCl has also been reported to give XTL.<sup>10</sup> Garten and Head measured photoemission during the XTL of NaCl over a range of different reagent concentrations, showing that each pulse of light ( $\sim 100$  ns) corresponded to a single nucleation event.<sup>11,12</sup>

Estimates of the nucleation rate predict exceedingly high local supersaturations  $S > 14$  ( $S = c/c_{\text{sat}}$ , where  $c_{\text{sat}}$  is the equilibrium saturation concentration for aqueous NaCl). Such high supersaturations are expected to be achieved where true homogeneous nucleation occurs in solution; the majority of nucleation studies are plagued by heterogeneous nucleation on “dust” that is exceedingly difficult to remove from solution. Based on their work, Garten and Head developed a picture of a disordered liquid-like cluster that “clicks-over” into crystalline form when it attains a critical size. Recent molecular dynamics simulations of nucleation lend some support to this picture of the nucleation mechanism.<sup>13,14</sup>

Bandrowski considered the XTL of sodium chloride to be due to electrical discharges resulting from the recombination of the ions, emitting an apparently blue–green light.<sup>5</sup> Weiser was the first to apply quantitative spectroscopic methods to the XTL of sodium chloride, by taking photographs with sensitive film.<sup>6,15</sup> Weiser found that there is a particular range of conditions where the rate of precipitation is optimal: if the mixing is carried out too fast, or the HCl is too concentrated, the XTL is weak. He ruled out CL as the cause of the XTL, since the rate of emission did not increase with the speed of precipitation, as would be expected for CL. He also ruled out TL by observing that stirring decreased the emission, rather than increasing it: increased emission would be expected due to the increased fracture rate of the crystals. Having optimized the experimental conditions, he used a series of colored filters and photographic film to determine the XTL spectrum, observing that the light was almost entirely emitted at wavelengths shorter than the indium blue line (451.1 nm).

The previous measurements of the XTL spectrum of NaCl are summarized in Fig. 1. As can be seen, the reports are conflicting and confusing, and this is largely due to the difficulty of measuring a spectrum from a very weak and transitory emission. The efforts of Longchambon are particularly worthy of commendation: by performing over 1500 precipitations, Longchambon obtained  $\sim 1$  h of exposure

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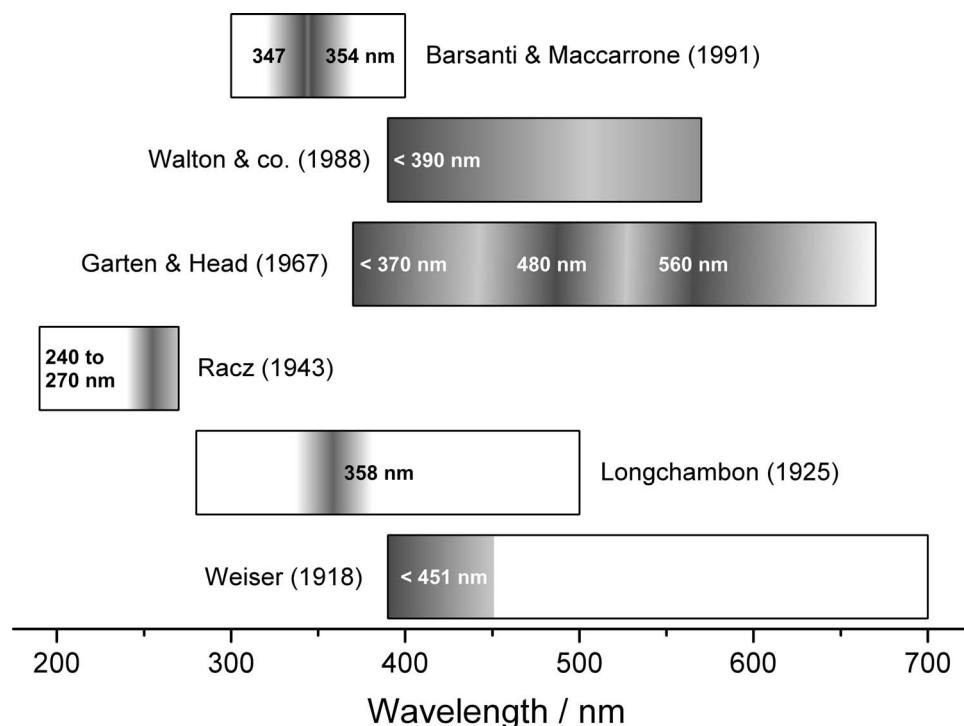


FIG. 1. Summary of studies of emission spectra from XTL of NaCl. In all cases, XTL was obtained by precipitation of near-saturated aqueous solutions of NaCl by mixing with concentrated HCl. Studies include those of Weiser,<sup>6</sup> Longchambon,<sup>16</sup> Racz,<sup>17</sup> Garten and Head,<sup>12</sup> Walton and co-workers,<sup>18</sup> and Barsanti and Maccarrone.<sup>1</sup> In earlier studies by Bandrowski and by Farnau, the colour of the XTL was reported to be “blue-green” and “bluish-white,” respectively.<sup>5,19</sup> The wavelength range of each study is shown by the box, the shaded region represents the emission range of XTL observed; wavelengths of nominal peaks are also noted. Two of the studies used intentional doping with metal cations, viz. Garten and Head ( $\text{Pb}^{2+}$ ) and Barsanti and Maccarrone ( $\text{Cu}^+$ ).

time on a photographic plate placed at the exit of a prism spectrograph.<sup>16</sup>

As early as 1913, Farnau suggested that impurities could be the cause of differences in the color of XTL observed by different investigators.<sup>19</sup> By using purified reagents, Garten and Head (1963) demonstrated that XTL emission from NaCl was observed *only* if the solutions contained small traces (ppm) of specific metal-ion impurities.<sup>12</sup> They found that some metals, such as  $\text{Pb}^{2+}$  and  $\text{Cu}^+$ , were highly active, whereas others, such as  $\text{Ni}^{2+}$  or  $\text{Ca}^{2+}$ , were not. Garten and Head also noted that most of the active cations also showed increased solubility in concentrated solutions of chloride, e.g., through formation of complexes such as  $\text{PbCl}_4^-$ . The work of Garten and Head clarified the huge variability in optimum conditions determined by previous authors: the purity of the reagents and the water used in different locations would be quite variable.

The most recent study of XTL of NaCl was that of Barsanti and Maccarrone, who used a photomultiplier tube coupled to a grating monochromator. The NaCl solution was intentionally doped with 630 ppm Cu impurities, and 100 repeat precipitations were carried out at 15 discrete points over the wavelength range of 300–400 nm.<sup>1</sup> The authors observed a broad emission from 320 to 370 nm, with peaks at 347 nm and 354 nm. The location of the peaks near 350 nm agreed with the known photoluminescence spectrum of NaCl crystals doped with  $\text{Cu}^+$ , which shows a single peak at 350 nm: the absence of two peaks as seen in the XTL spectrum was

attributed to the higher Cu concentrations used for the photoluminescence measurements.

At the present time it is still not clear if dopant metal ions promote the XTL, perhaps by promoting triboluminescence resulting from fracture of nascent crystallites, or if the dopant is the sole emission center. A number of factors have contributed to the apparently contradictory results reported in the literature for XTL of NaCl, and we summarize them as follows:

1. Regular borosilicate glass is strongly absorbing in the UV region (transmission only  $\sim 10\%$  at 300 nm). This would limit most studies—perhaps inadvertently—to measurements above 300 nm;
2. The intensities are so low, and duration so short, that even photomultiplier methods require repeat measurements and long integration times;
3. The importance of metal-ion impurities was not fully appreciated until the work of Garten and Head;
4. The only deep-UV study was limited to the region 190–270 nm; other photomultiplier methods have been limited to measuring a handful of discrete points in narrow windows in the UV–visible spectrum.

In the present article, we present the first, fully dispersed spectra of XTL from the deep UV to visible region (190–650 nm). The spectra allow us to determine the mechanism for XTL of NaCl unambiguously for the first time, an effect that has intrigued chemists and physicists for over a century.



## II. EXPERIMENTAL

The XTL of NaCl can be obtained by adding a solution of concentrated HCl to a nearly saturated solution of NaCl that has been doped with the salt of an impurity cation. We found that the published recipes for XTL gave highly variable results. In some tests only a few flashes were observed, and in other cases none at all. Repeatability was very poor, and even doping with metal cations, such as  $\text{Ag}^+$ , did not produce consistent results. It is clear that the method of mixing is very important: the solutions must be mixed quickly, but not too briskly. The shape of the sample tube was also found to be important, presumably because it affects the rate of mixing. After some experimentation, we found that the best results were obtained by doping the NaCl solution with  $\text{Ag}^+$ , and additionally doping the HCl solution with another metal cation, such as  $\text{Cu}^{2+}$ . Our choice of metal dopants was made based on previous work.<sup>1,12</sup> Garten and Head observed good XTL using either  $\text{Pb}^{2+}$  or  $\text{Ag}^+$  dopants. Barsanti and Maccarrone found that  $\text{Ag}^+$  produced more intense XTL than  $\text{Cu}^+$  by a factor of  $\sim 10$ , although the cause for this was not investigated further. Garten and Head noted that the time dependence of light pulses varied somewhat with the dopant, and posited that this was due to different emitters: either from single nuclei or grape-like groups of nuclei.<sup>12</sup> In previous works, however, only single dopants were tested; our goal for the present work was to maximize the XTL intensity.

Deionized water (Fisher, HPLC grade) was used to prepare all solutions and for rinsing glassware. Stock solutions of HCl (24 wt. %) and nearly saturated aqueous NaCl ( $S = 0.98$  at  $20^\circ\text{C}$ ) were prepared from conc. HCl (Fisher, AR Grade, 36%) and solid NaCl (Sigma-Aldrich, Reagent-Plus  $\geq 99.5\%$ ), respectively. A stock solution of 0.070 M silver nitrate was prepared, to be used as one of the additives to promote crystallization. Stock solutions of dopant cations, which act as activators for the XTL,<sup>12</sup> were also prepared: 0.050 M copper(II) sulphate and 0.062 M dysprosium(III) chloride. In order to detect deep-UV emission, fused-silica test tubes (16 mm  $\times$  150 mm) were employed. In the first tube (solution 1) was placed 10 ml of the stock HCl solution, to which was added 0.05 ml of the metal-ion stock solution. In the second tube (solution 2) was placed 10 ml of stock NaCl solution, to which was added 0.5 ml of the  $\text{AgNO}_3$  solution. On addition of the  $\text{AgNO}_3$ , a small amount of AgCl precipitate was formed, which was removed by shaking and a few seconds of ultrasonication in a bath. Although AgCl is very insoluble in water ( $\text{p}K_{\text{sp}} = 9.75$ ), we note that the solubility of  $\text{Ag}^+$  at high  $\text{Cl}^-$  concentrations is much greater due to formation of the soluble complex species  $\text{AgCl}_2^-$ ,  $\text{AgCl}_3^{2-}$ , and  $\text{AgCl}_4^{3-}$ . For our nearly saturated NaCl solution we estimate the solubility of  $\text{Ag}^+$  to be  $5.3 \times 10^{-2}$  M,<sup>20</sup> and we do not believe that solid AgCl plays a role in the XTL.

We calculate the resulting concentrations in the final (mixed) solution as  $[\text{Dy}^{3+}] = 1.4 \times 10^{-4}$  M,  $[\text{Cu}^{2+}] = 1.2 \times 10^{-4}$  M, and  $[\text{Ag}^+] = 1.7 \times 10^{-3}$  M. To aid comparison against previous work, we give the concentration of dopants as mole fractions relative to  $\text{Na}^+$  as follows: 658 ppm  $\text{Ag}^+/\text{Na}^+$ , 58 ppm  $\text{Dy}^{3+}/\text{Na}^+$ , and 47 ppm  $\text{Cu}^{2+}/\text{Na}^+$ .

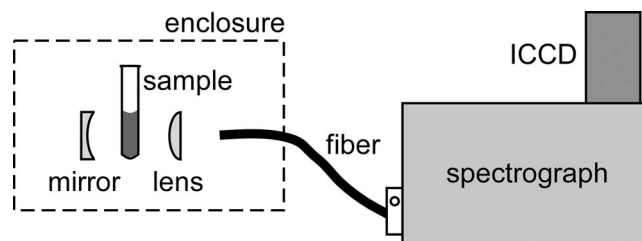


FIG. 2. Schematic diagram illustrating the experimental apparatus. The sample was mixed in a tube held between a mirror and a lens. Light is collected onto one end of a fiber-optic bundle; the other end was connected to the input slit of the commercial spectrograph. The detector is an intensified charge-couple device (ICCD). The light-collection setup was covered in a dark enclosure (shown by the dashed line). The lens, fiber, and sample tube were made of UV-grade fused silica, and the mirror had a broad-band UV-visible enhanced-aluminium coating.

The spectrometer used was an Acton 320PI (Princeton Instruments), with a 1 m UV fiber-optic bundle coupled to the entrance slit of the spectrometer: see Fig. 2. The array detector was an intensified charge-coupled device (ICCD). Two gratings were used, having 300 and 600 grooves  $\text{mm}^{-1}$ . The 300  $\text{mm}^{-1}$  grating allowed us to observe almost the entire deep-UV to visible region ( $\sim 500$  nm) in single experiments; the 600  $\text{mm}^{-1}$  grating gave a shorter wavelength range ( $\sim 100$  nm) and was used to verify that no finer underlying structure could be resolved. The wavelength was calibrated using gas discharges in air and argon. The XTL was collected at the input end of the fiber using a 50 mm diameter plano-convex fused-silica lens ( $f = +63$  mm). The collection was improved by placing a 50 mm diameter concave mirror ( $f = +50$  mm, enhanced-Al coating,  $R > 85\%$ , 250–500 nm)  $\sim 50$  mm behind the XTL tube. The wavelength sensitivity of the system was found to peak in the deep UV (200–250 nm) and is broadly flat (within a factor of 2) in the UV–visible region (250–650 nm). The spectra presented here have not been corrected for wavelength sensitivity. The entire light-collection setup was covered by blackout material, and the experiments were conducted in a darkened room. Spectra of the XTL were obtained by integrating the emission in sets of 5 s, at 95% gain of the detector.

The test tube containing solution 1 was fixed in place between the lens and the mirror, and solution 2 was poured rapidly but smoothly into solution 1. Within about 10 s the XTL begins, and can be seen as numerous bright flashes of light occurring throughout the solution. The XTL was observed to last  $\sim 2$  min, steadily decreasing in intensity. Salt crystals dropped to the bottom of the tube.

## III. RESULTS

We believe that one of the successful features of our recipe is the higher proportion of  $\text{Ag}^+$  compared to previous studies, which promotes a very high initial rate of nucleation, and hence XTL emission. The XTL was bright enough to capture using a simple compact digital camera, as shown in Fig. 3.

The emission spectrum for NaCl doped with  $\text{Dy}^{3+}$  is shown in Fig. 4, and the data have been fitted with a set of

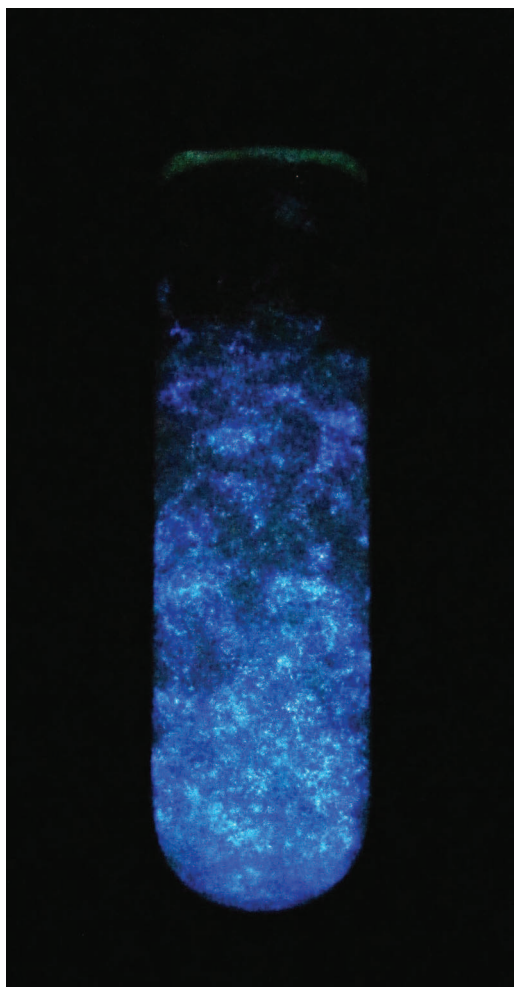


FIG. 3. Image of XTL of NaCl captured using a compact digital camera (Canon PowerShot S90, ISO 3200, 0.5 s exposure,  $f/2$  aperture). The metal dopant used was  $\text{Cu}^{2+}$ . This picture has been enhanced to improve contrast. The outline of the round-bottom tube can be seen clearly, as can the meniscus of the solution at the top. The XTL appears as rapid, localized flashes.

Gaussian functions giving peaks at 253, 267, 409, and 504 nm. The choice and number of Gaussian functions for fitting was arbitrary, and used only to assist in identifying possible components in the spectrum. The XTL spectrum for NaCl doped with  $\text{Cu}^{2+}$  is shown in Fig. 5, with peaks at 252, 259, 359, and 424 nm. These spectra represent a substantial improvement over previous XTL spectra, with clearly defined bands and some features that are shared between the doped systems.

The largest peak at 250 nm with a smaller shoulder at 260 nm can be seen in both spectra, and these peaks can be attributed to the  $4d^9 5s^1 \rightarrow 4d^{10}$  electronic emission of  $\text{Ag}^+$  in NaCl. As discussed below, the luminescence of this emission has been studied extensively in crystalline  $\text{NaCl}:\text{Ag}^+$  by photoexcitation of the so-called A and B bands at 210 and 217 nm. The position and width of the XTL features are identical to the photoemission spectra at room temperature.<sup>21,22</sup>

The other peak that appears in both XTL spectra is the broad feature at 415 nm. The peak wavelength of this feature is similar to an emission seen in the TL spectrum of NaCl at 440 nm, which Walton attributed to black-body radiation in

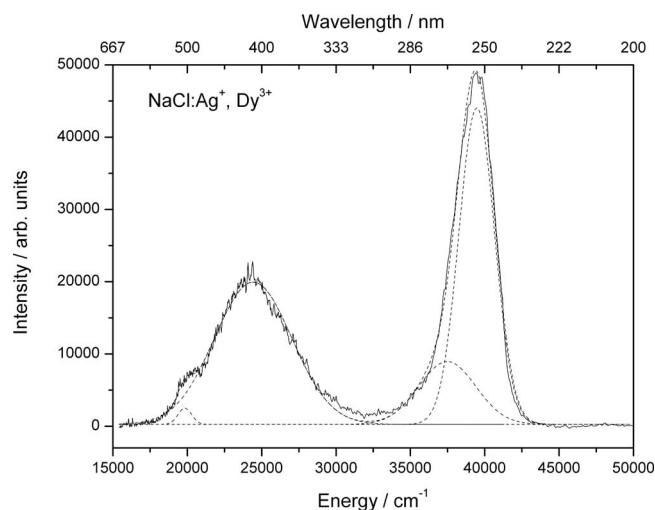


FIG. 4. XTL emission spectrum for NaCl doped with  $\text{Dy}^{3+}$ . The experimental data (solid line) have been fitted with a set of Gaussian functions (dashed lines) giving 4 peaks at  $253 \pm 8$ ,  $267 \pm 14$ ,  $409 \pm 44$ , and  $504 \pm 12$  nm.

the visible region.<sup>23</sup> Such an emission would indicate a XTL emission mechanism that is native to NaCl, i.e., does not depend on impurity cations. From the Planck energy distribution equation, it can be shown that black-body radiation at 6600 K peaks at 440 nm with a full-width at half-maximum of 245 nm, much wider than observed in our XTL spectrum: therefore, we rule out TL as the cause. Instead, the feature at  $\sim 415$  nm is attributed to  $(\text{Ag}^+)_2$  pairs in the NaCl lattice, and we note that the energy and width of the XTL emission are almost identical to that observed by Etzel *et al.* in the fluorescence spectrum for  $(\text{Ag}^+)_2$ .<sup>21,22</sup> Pedrini *et al.* also identified a previously unseen green fluorescent feature at  $\sim 500$  nm that they attributed to  $(\text{Ag}^+)_2$ , and this would account for the very small peak at 504 nm in Fig. 4.<sup>24</sup> In Figs. 4 and 5 there may be some evidence for an additional, much weaker emission near 300 nm, which could also be attributed to  $(\text{Ag}^+)_2$ .<sup>24</sup> The peak at 500 nm is not seen clearly in Fig. 5, although this may be

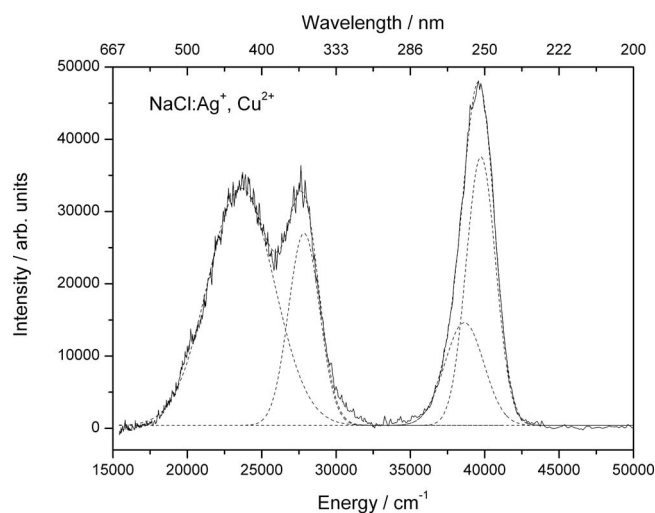


FIG. 5. XTL emission spectrum for NaCl doped with  $\text{Cu}^{2+}$ . The experimental data (solid line) have been fitted with a set of Gaussian functions (dashed lines) giving 4 peaks at  $252 \pm 6$ ,  $259 \pm 9$ ,  $359 \pm 14$ , and  $424 \pm 40$  nm.

due to it being swamped by the more intense blue emission at 424 nm. Luminescence for NaCl:Dy<sup>3+</sup> has been reported to give peaks at 480, 585, and 670 nm:<sup>25</sup> since we see no evidence for features near 585 and 670 nm in Fig. 4, we rule out XTL emission from Dy<sup>3+</sup> centers as the cause of the XTL peak at 504 nm.

The XTL spectrum for NaCl:Ag<sup>+</sup>,Cu<sup>2+</sup> shows a unique feature at 359 nm, which we attribute to the  $3d^9 4s^1 \rightarrow 3d^{10}$  electronic emission of Cu<sup>+</sup> in NaCl, analogous to the emission of Ag<sup>+</sup> at 250 nm. Emission from Cu<sup>+</sup> suggests that the XTL environment is reducing: this may be due to release of trapped electrons during the crystalline phase transition. As for the case of Ag<sup>+</sup>, we find that the width of the Cu<sup>+</sup> emission feature is identical to luminescence measurements at room temperature.<sup>1,26</sup>

#### IV. DISCUSSION

The photoluminescence of Cu<sup>+</sup> and Ag<sup>+</sup> substituents in NaCl have been studied extensively.<sup>27</sup> The crystal radius of Ag<sup>+</sup> (1.0 Å) is almost identical to Na<sup>+</sup> (0.99 Å).<sup>28</sup> The partial charge forecast model developed by Bosi and Nimis,<sup>29,30</sup> and electronic structure calculations of Pedrini *et al.*,<sup>31</sup> indicate that in the ground electronic state, the Ag<sup>+</sup> ion substitutes on center for a Na<sup>+</sup> ion. The absorption spectrum of NaCl:Ag<sup>+</sup> consists of a series of broad bands labelled A to F, ranging from 220 to 180 nm. The absorptions are parity forbidden in the free Ag<sup>+</sup> ion, but become partially allowed by coupling to lattice vibrations with odd symmetry.

The emission at 250 nm, as seen in the XTL spectrum, originates from the lowest triplet states (<sup>3</sup>E<sub>g</sub>) that are split by spin-orbit coupling into the upper <sup>3</sup>E<sub>g</sub>(T<sub>2g</sub>) and lower <sup>3</sup>E<sub>g</sub>(T<sub>1g</sub>) states. Both transitions are partially parity-allowed: the <sup>3</sup>E<sub>g</sub>(T<sub>2g</sub>) → <sup>1</sup>A<sub>1g</sub> is partially spin-allowed, but the <sup>3</sup>E<sub>g</sub>(T<sub>1g</sub>) → <sup>1</sup>A<sub>1g</sub> transition is spin-forbidden.<sup>32,33</sup> The two <sup>3</sup>E<sub>g</sub> states are found to be close in energy,  $\Delta \approx 80 \text{ cm}^{-1}$ , which causes a temperature-dependent lifetime of the luminescence decay.<sup>27,30,33,34</sup> For NaCl:Ag<sup>+</sup>, the measured lifetimes are 18.6 μs and 0.31 ms for the partially spin-allowed [<sup>3</sup>E<sub>g</sub>(T<sub>2g</sub>) → <sup>1</sup>A<sub>1g</sub>] and spin-forbidden [<sup>3</sup>E<sub>g</sub>(T<sub>1g</sub>) → <sup>1</sup>A<sub>1g</sub>] transitions, respectively. The lower <sup>3</sup>E<sub>g</sub>(T<sub>1g</sub>) state is sometimes referred to as metastable.

The two Gaussian functions we used to fit the XTL emission (at 250 and 260 nm, see Figs. 4 and 5) are separated by a large amount (~10 nm, ~1000 cm<sup>-1</sup>) compared to the separation as determined from measurements of the luminescence lifetime (~0.5 nm, ~80 cm<sup>-1</sup>). Therefore, the smaller peak at 260 nm is not due to emission from the lower <sup>3</sup>E<sub>g</sub> state, but represents a tail in the emission from the unresolved <sup>3</sup>E<sub>g</sub> transitions. The analogous emission for Cu<sup>+</sup> at 359 nm is also expected to be asymmetric. This tail at longer wavelengths can be explained by the offset between the minima in the excited (<sup>3</sup>E<sub>g</sub>) and ground (<sup>1</sup>A<sub>1g</sub>) potential energy curves, as illustrated in Fig. 6.<sup>31</sup>

Barsanti and Maccarrone speculated that, compared to the photoluminescence spectra, the XTL emission features would be shifted to longer wavelengths, or would show an enhanced tail at longer wavelengths.<sup>1</sup> This might occur due to emission at longer reaction co-ordinates during the col-

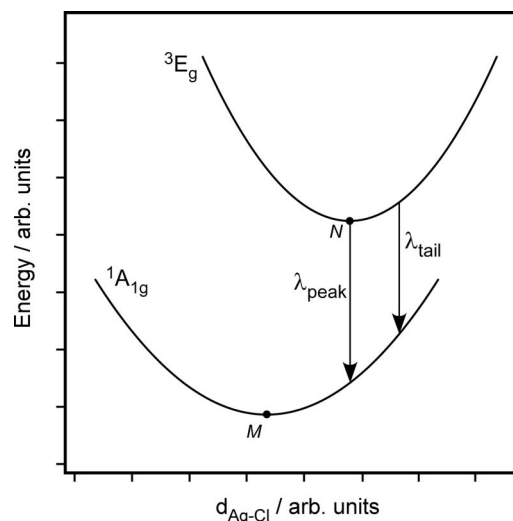


FIG. 6. Schematic diagram illustrating the shapes of the ground (<sup>1</sup>A<sub>1g</sub>) and low-lying excited triplet (<sup>3</sup>E<sub>g</sub>) potential energy surfaces of NaCl:Ag<sup>+</sup> as a function of the Ag–Cl bond length ( $d_{\text{Ag-Cl}}$ ). This figure is based on electronic structure calculations (MSXα) of (AgCl<sub>6</sub>)<sup>5-</sup> by Pedrini *et al.*<sup>31</sup> The bond-length coordinate can be imagined to be representative of the reaction coordinate during collapse of a cluster during the XTL nucleation event. The similarities between the XTL and photoluminescence spectra suggest, however, that the timescale for XTL emission from the <sup>3</sup>E<sub>g</sub> states is much slower than the re-organization of the cluster; the emission then takes place near the equilibrated crystalline geometry, i.e., the minimum of the excited PES (point N). The long-wavelength tail in the emission ( $\lambda_{\text{tail}}$ ) results from the displacement between the minima in the ground and excited states.

lapse of the cluster into crystalline form. We find, however, that the shape of the Ag<sup>+</sup> emission feature is identical to the photoluminescence emission reported by Etzel.<sup>21</sup> Moreover, we see no evidence for emission from higher electronic excited states, in particular, from singlet states where the transitions are spin-allowed. It seems more likely, therefore, that the clusters first collapse to a crystalline phase on a very short timescale, with relaxation of the dopant cation to the lowest triplet electronic states. Transition from the lowest excited <sup>3</sup>E<sub>g</sub> states to the ground electronic state of the cation in the nascent crystal results in the observed emission. Relaxation to the lowest triplet states could occur by efficient nonadiabatic transitions during collapse. This distinct sequence of events during nucleation fits well with the long lifetimes of the excited <sup>3</sup>E<sub>g</sub> states. Our mechanism is also in accord with the measurements of Garten and Head, who observed that emissions from XTL of NaCl doped with Ag<sup>+</sup> occur as distinct trains of pulses, ~100 μs long, which decay monotonically in intensity.<sup>11,12</sup>

As discussed above, the features at 415 nm (blue) and 504 nm (green) can be attributed to (Ag<sup>+</sup>)<sub>2</sub> pairs. Luminescence of this type can be excited in crystals of NaCl:Ag<sup>+</sup> via the A\* absorption band at 227 nm, which only appears at higher Ag<sup>+</sup> concentrations. Etzel *et al.* and Pedrini *et al.* demonstrated that the intensity of the blue emission scales with the concentration of (Ag<sup>+</sup>)<sub>2</sub> pairs that would be expected if the Ag<sup>+</sup> ions occupy cation sites at random.<sup>22,35</sup> By measuring the polarization of the photoluminescence, Pedrini *et al.* determined that both the blue and green emissions are parallel to the C<sub>4</sub> axis of the NaCl crystal.<sup>24</sup> The blue emission is thought most likely

due to  $\text{Ag}^+$  ions occupying two adjacent  $\text{Na}^+$  sites, separated by a  $\text{Cl}^-$  anion or a vacancy; the green emission is thought to be associated with a similar configuration of  $\text{Ag}^+$  cations in proximity to a vacancy, possibly off-axis.<sup>35</sup> It might be expected that collapse of a non-crystalline cluster would trap a lot of vacancy defects, which could explain the relatively intense emission from the blue feature. Finally, we note that emissions like the blue feature are likely to be responsible for a large fraction of the XTL of NaCl that was observed by eye in historical reports.

## V. CONCLUSIONS

In summary, a protocol for producing intense XTL in NaCl was developed and used to record complete, fully dispersed deep UV–visible spectra (200–650 nm) of XTL for the first time. We show conclusively that the XTL of NaCl is due to emission from luminescent substituent cations in the crystal lattice, and is not due to NaCl itself, e.g., triboluminescence resulting from crystalline fracture. The results represent the culmination of over a century of interest and speculation as to the nature of XTL of NaCl.

The nature of the electronic transitions for  $\text{Ag}^+$  and  $\text{Cu}^+$  that contributed to the observed XTL spectra has been discussed in detail. We see no evidence for emission from non-equilibrium configurations or higher electronic states during collapse of a cluster to a crystalline nucleus. The results suggest that the transformation to crystalline phase occurs rapidly, with efficient relaxation to the lowest electronic states of the substituent cation. Subsequent emission from these excited states of the cation in the nascent crystal results in the observed emission.

The effect of XTL has the potential to act as a signal of the critical act of homogeneous nucleation in solution, which experiment and theory still struggle to understand. We hope that our work will stimulate a new generation of experiments in this area.

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- <sup>1</sup>M. Barsanti and F. Maccarrone, *Riv. Nuovo Cimento* **14**(6), 1 (1991).
- <sup>2</sup>Y. Tsuboi, T. Seto, S. Ishizaka, and N. Kitamura, *J. Phys. Chem. B* **108**(9), 2822 (2004).
- <sup>3</sup>J. I. Zink and B. P. Chandra, *J. Phys. Chem.* **86**(1), 5 (1982).
- <sup>4</sup>E. N. Harvey, *A History of Luminescence from the Earliest Times until 1900* (American Philosophical Society, Philadelphia, 1957).
- <sup>5</sup>E. Bandrowski, *Z. Phys. Chem.* **15**, 323 (1894).
- <sup>6</sup>H. B. Weiser, *J. Phys. Chem.* **22**, 480 (1918).
- <sup>7</sup>J. W. Mullin, *Crystallization*, 4th ed. (Butterworth-Heinemann, Oxford, 2001).
- <sup>8</sup>T. A. Ring, *Adv. Colloid Interface Sci.* **91**(3), 473 (2001).
- <sup>9</sup>S. N. White, A. D. Chave, and G. T. Reynolds, *J. Geophys. Res.* **107**(B1), 2001, doi:10.1029/2000JB000015 (2002).
- <sup>10</sup>K. Jablczynski and A. Cholewicki, *Rocz. Chem.* **17**, 387 (1937).
- <sup>11</sup>V. A. Garten and R. B. Head, *Philos. Mag.* **14**, 1243 (1966).
- <sup>12</sup>V. A. Garten and R. B. Head, *Philos. Mag.* **8**(95), 1793 (1963).
- <sup>13</sup>D. Zahn, *Phys. Rev. Lett.* **92**, 040801 (2004).
- <sup>14</sup>J. D. Shore, D. Perchak, and Y. Schmidman, *J. Chem. Phys.* **113**, 6276 (2000).
- <sup>15</sup>H. B. Weiser, *J. Phys. Chem.* **22**, 576 (1918).
- <sup>16</sup>H. Longchambon, *Bull. Soc. Fr. Mineral.* **48**, 130 (1925).
- <sup>17</sup>C. Racz, *J. Chim. Phys. Phys.-Chim. Biol.* **40**, 5 (1943).
- <sup>18</sup>M. A. Gibbon, H. Sopp, J. Swanson, and A. J. Walton, *J. Phys. C* **21**, 1921 (1988).
- <sup>19</sup>E. F. Farnau, *J. Phys. Chem.* **17**, 637 (1913).
- <sup>20</sup>R. de Levie, *How to Use Excel in Analytical Chemistry and in General Scientific Data Analysis* (Cambridge University Press, Cambridge, England, 2001).
- <sup>21</sup>H. W. Etzel and J. H. Schulman, *J. Chem. Phys.* **22**(9), 1549 (1954).
- <sup>22</sup>H. W. Etzel, J. H. Schulman, R. J. Ginther, and E. W. Claffy, *Phys. Rev.* **85**(6), 1063 (1952).
- <sup>23</sup>A. J. Walton, *Adv. Phys.* **26**(6), 887 (1977).
- <sup>24</sup>C. Pedrini, B. Atoussi, H. Chermette, and B. Moine, *J. Lumin.* **31-32**, 330 (1984).
- <sup>25</sup>V. F. Pissarenko and S. V. Voropaeva, *Phys. Status Solidi* **15**(2), K95 (1966).
- <sup>26</sup>R. R. Patil and S. V. Moharil, *J. Lumin.* **63**(5-6), 339 (1995).
- <sup>27</sup>L. Bosi, F. L. Bosi, D. Gallo, and M. Zelada, *Phys. Status Solidi B* **223**(3), 821 (2001).
- <sup>28</sup>in *CRC Handbook of Chemistry and Physics*, edited by W. M. Haynes (CRC, Boca Raton, FL, 2011).
- <sup>29</sup>L. Bosi and M. Nimis, *Nuovo Cimento D* **13**(3), 377 (1991).
- <sup>30</sup>L. Bosi and M. Zelada, *Chem. Phys. Lett.* **284**(5-6), 382 (1998).
- <sup>31</sup>C. Pedrini, H. Chermette, A. B. Goldberg, D. S. McClure, and B. Moine, *Phys. Status Solidi B* **120**(2), 753 (1983).
- <sup>32</sup>H. Chermette and C. Pedrini, *J. Chem. Phys.* **75**(4), 1869 (1981).
- <sup>33</sup>C. Pedrini and B. Jacquier, *J. Phys. C* **13**(25), 4791 (1980).
- <sup>34</sup>L. Bosi, D. Gallo, and M. Zelada, *Chem. Phys. Lett.* **251**(5-6), 335 (1996).
- <sup>35</sup>B. Atoussi, C. Pedrini, B. Moine, and C. Madej, *Phys. Status Solidi B* **128**(2), 683 (1985).